

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 November 2004 (04.11.2004)

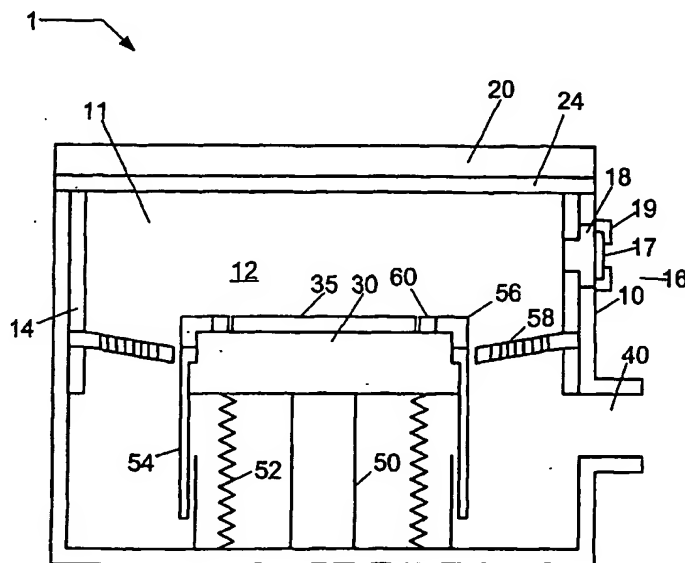
PCT

(10) International Publication Number
WO 2004/095532 A2

- (51) International Patent Classification⁷: **H01L** (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (21) International Application Number: PCT/US2004/006080
- (22) International Filing Date: 18 March 2004 (18.03.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/458,439 31 March 2003 (31.03.2003) US
- (71) Applicant (for all designated States except US): **TOKYO ELECTRON LIMITED [JP/JP]**; TBS Broadcast Center, 3-6, Akasak 5-chome, Minato-ku, Tokyo 107-8481 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **ESCHER, Gary** [US/US]; 29 Gallant Drive, Hampstead, NH 03841 (US). **ALLEN, Mark, A.** [US/US]; 18 Winthrop Street, Essex, ME 01929 (US).
- (74) Agent: **MAIER, Gregory, J.**; Oblon, Spivak, McClelland, Maier & Neustadt, P.C., 1940 Duke Street, Alexandria, VI 22314 (US).
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: A BARRIER LAYER FOR A PROCESSING ELEMENT AND A METHOD OF FORMING THE SAME



(57) Abstract: In order to mitigate erosion of exposed processing elements in a processing system by the process and any subsequent contamination of the substrate in the processing system, processing elements exposed to the process are coated with a protective barrier. The protective barrier comprises a protective layer that is resistant to erosion by the plasma, and a bonding layer that improves the adhesion of the protective layer to the processing element to mitigate possible process contamination by failure of the protective layer.

WO 2004/095532 A2



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

A BARRIER LAYER FOR A PROCESSING ELEMENT AND A METHOD OF FORMING THE SAME

Cross Reference to Related Applications

[0001] This application claims priority to and is related to U.S. Provisional Application Serial No. 60/458,439, filed on March 31, 2003. The contents of this application is incorporated herein by reference.

Field of the Invention

[0002] The present invention relates to a barrier layer for a processing element and a method of forming the same, and more particularly to a barrier layer for a processing element comprising an adhesion layer and a protective layer and a method of forming the same.

Background of the Invention

[0003] The fabrication of integrated circuits (IC) in the semiconductor industry typically employs plasma to create and assist surface chemistry within a plasma reactor necessary to remove material from and deposit material to a substrate. In general, plasma is formed within the plasma reactor under vacuum conditions by heating electrons to energies sufficient to sustain ionizing collisions with a supplied process gas. Moreover, the heated electrons can have energy sufficient to sustain dissociative collisions and, therefore, a specific set of gases under predetermined conditions (e.g., chamber pressure, gas flow rate, etc.) are chosen to produce a population of charged species and chemically reactive species suitable to the particular process being performed within the chamber (e.g., etching processes where materials are removed from the substrate or deposition processes where materials are added to the substrate).

[0004] Although the formation of a population of charged species (ions, etc.) and chemically reactive species is necessary for performing the function of

the plasma processing system (i.e. material etch, material deposition, etc.) at the substrate surface, other component surfaces on the interior of the processing chamber are exposed to the physically and chemically active plasma and, in time, can erode. The erosion of exposed components in the plasma processing system can lead to a gradual degradation of the plasma processing performance and ultimately to complete failure of the system.

[0005] In order to minimize the damage sustained by exposure to the processing plasma, components of the plasma processing system, known to sustain exposure to the processing plasma, are coated with a protective barrier. For example, components fabricated from aluminum can be anodized to produce a surface layer of aluminum oxide, which is more resistant to the plasma. In another example, a consumable or replaceable component, such as one fabricated from silicon, quartz, alumina, carbon, or silicon carbide, can be inserted within the processing chamber to protect the surfaces of more valuable components that would impose greater costs during frequent replacement. Furthermore, it is desirable to select surface materials that minimize the introduction of unwanted contaminants, impurities, etc. to the processing plasma and possibly to the devices formed on the substrate.

[0006] In both cases, the inevitable failure of the protective coating, either due to the integrity of the protective barrier or the integrity of the fabrication of the protective barrier, and the consumable nature of the replaceable components demands frequent maintenance of the plasma processing system. This frequent maintenance can produce costs associated with plasma processing down-time and new plasma processing chamber components, which can be excessive.

Summary of the Invention

[0007] A barrier layer and a method of forming the same is described.

[0008] A protective barrier on a processing element utilized in a processing system for performing a process comprising: a bonding layer coupled to the processing element, wherein the bonding layer comprises a layer formed using plasma electrolytic oxidation; and a protective layer coupled to the bonding layer and configured to be exposed to the process.

[0009] A method of forming a protective barrier on a processing element utilized in a processing system for performing a process comprising: applying a bonding layer to the processing element, wherein the application of the bonding layer comprises plasma electrolytic oxidation; and applying a protective layer to the bonding layer.

Brief Description of the Drawings

[0010] These and other advantages of the invention will become more apparent and more readily appreciated from the following detailed description of the exemplary embodiments of the invention taken in conjunction with the accompanying drawings, where:

[0011] FIG. 1 illustrates a schematic block diagram of a plasma processing system according to an embodiment of the present invention;

[0012] FIG. 2 presents an expanded cross-sectional view of a portion of a processing element in a plasma processing system as shown in FIG. 1; and

[0013] FIG. 3 presents a method of forming a protective layer on a processing element in a plasma processing system according to an embodiment of the present invention.

Detailed Description of an Embodiment

[0014] A plasma processing system 1, such as one capable of plasma etching, is depicted in FIG. 1 comprising a processing chamber 10, an upper assembly 20, an upper wall 24, a substrate holder 30 for supporting a substrate 35, and a pumping duct 40 coupled to a vacuum pump (not shown) for providing a reduced pressure atmosphere 11 in processing chamber 10. Processing chamber 10 can, for example, facilitate the formation of a processing plasma in a process space 12 adjacent substrate 35. The plasma processing system 1 can be configured to process various substrates (i.e. 200 mm substrates, 300 mm substrates, or larger).

[0015] In the illustrated embodiment, upper assembly 20 can comprise at least one of a cover, a gas injection assembly, and an upper electrode impedance match network. For example, the upper wall 24 can, for example,

be configured to comprise an electrode having an electrode plate that is coupled to a radio frequency (RF) source, and therefore facilitate an upper electrode for the plasma processing system 1. In another alternate embodiment, the upper assembly 20 comprises a cover and an upper wall 24, wherein the upper wall 24 is maintained at an electrical potential equivalent to that of the processing chamber 10. For example, the processing chamber 10, the upper assembly 20, and the upper wall 24 can be electrically connected to ground potential, and facilitate a grounded wall for the plasma processing system 1.

[00016] Processing chamber 10 can, for example, further comprise a deposition shield 14 for protecting the plasma processing chamber 10 from the processing plasma in the process space 12, and an optical viewport 16. Optical viewport 16 can comprise an optical window 17 coupled to the backside of an optical window deposition shield 18, and an optical window flange 19 can be configured to couple optical window 17 to the optical window deposition shield 18. Sealing members, such as O-rings, can be provided between the optical window flange 19 and the optical window 17, between the optical window 17 and the optical window deposition shield 18, and between the optical window deposition shield 18 and the processing chamber 10. Optical window deposition shield 18 can extend through an opening 70 within deposition shield 14. Optical viewport 16 can, for example, permit monitoring of optical emission from the processing plasma in process space 12.

[00017] Substrate holder 30 can, for example, further comprise a vertical translational device 50 surrounded by a bellows 52 coupled to the substrate holder 30 and the processing chamber 10, and configured to seal the vertical translational device 50 from the reduced pressure atmosphere 11 in processing chamber 10. Additionally, a bellows shield 54 can, for example, be coupled to the substrate holder 30 and configured to protect the bellows 52 from a processing plasma. Alternately, substrate holder does not comprise a vertical translational device and bellows.

[00018] Substrate holder 10 can further be coupled to a focus ring 60, and, optionally, a shield ring 56. Furthermore, a baffle plate 58 can, for example, extend about a periphery of the substrate holder 30.

[00019] Substrate 35 can be, for example, transferred into and out of processing chamber 10 through a slot valve (not shown) and chamber feed-through (not shown) via robotic substrate transfer system where it is received by substrate lift pins (not shown) housed within substrate holder 30 and mechanically translated by devices housed therein. Once substrate 35 is received from the substrate transfer system, it is lowered to an upper surface of substrate holder 30.

[00020] Substrate 35 can be, for example, affixed to the substrate holder 30 via an electrostatic clamping system. Furthermore, substrate holder 30 can, for example, further include a cooling system including a re-circulating coolant flow that receives heat from substrate holder 30 and transfers heat to a heat exchanger system (not shown), or when heating, transfers heat from the heat exchanger system to substrate holder 30. Moreover, gas can, for example, be delivered to the back-side of substrate 35 via a backside gas system to improve the gas-gap thermal conductance between substrate 35 and substrate holder 30. Such a system can be utilized when temperature control of the substrate is required at elevated or reduced temperatures. In other embodiments, heating elements, such as resistive heating elements, or thermo-electric heaters/coolers can be included.

[00021] In the illustrated embodiment, shown in FIG. 1, substrate holder 30 can comprise an electrode (not shown) through which RF power is coupled to the processing plasma in process space 12. For example, substrate holder 30 can be electrically biased at a RF voltage via the transmission of RF power from a RF generator (not shown) through an impedance match network (not shown) to substrate holder 30. The RF bias can serve to heat electrons to form and maintain plasma. In this configuration, the system can operate as a reactive ion etch (RIE) reactor, wherein the chamber and upper gas injection electrode serve as ground surfaces. A typical frequency for the RF bias can range from 1 MHz to 100 MHz, for example, 13.56 MHz. RF systems for plasma processing are well known to those skilled in the art.

[00022] Alternately, the processing plasma formed in process space 12 can be formed using a parallel-plate, capacitively coupled plasma (CCP) source, an inductively coupled plasma (ICP) source, transformer coupled plasma (TCP) source, any combination thereof, and with and without DC magnet

systems. Alternately, the processing plasma in process space 12 can be formed using electron cyclotron resonance (ECR). In yet another embodiment, the processing plasma in process space 12 is formed from the launching of a Helicon wave. In yet another embodiment, the processing plasma in process space 12 is formed from a propagating surface wave.

[00023] Referring still to FIG. 1, plasma processing device 1 comprises one or more processing elements, each of which can be exposed to the processing plasma in process space 12, and are, therefore, subject to potential erosion during processing. For example, the one or more processing elements can comprise an electrode plate, a deposition shield, a chamber liner, a bellows shield, a baffle plate, an optical window deposition shield, a shield ring, a focus ring, etc. In order to mitigate erosion of the exposed processing elements by the processing plasma and any subsequent contamination of the substrate, the processing elements are coated with a protective barrier.

[00024] In an embodiment, as depicted in FIG. 2, a processing element 100 comprises a protective barrier 110 having a protective layer 120 that is resistant to erosion by the plasma, and a bonding layer 130 that improves the adhesion of the protective layer 120 to the processing element 100 to mitigate possible process contamination by failure of the protective layer.

[00025] The protective layer 120 can, for example, comprise at least one of Al_2O_3 and Y_2O_3 . In another embodiment of the present invention, the protective layer comprises at least one of a III-column element (column III of periodic table) and a Lanthanone element. In another embodiment of the present invention, the III-column element comprises at least one of Yttrium, Scandium, and Lanthanum. In another embodiment of the present invention, the Lanthanone element comprises at least one of Cerium, Dysprosium, and Europium. In another embodiment of the present invention, the compound forming protective layer comprises at least one of Ytria (Y_2O_3), Sc_2O_3 , Sc_2F_3 , YF_3 , La_2O_3 , CeO_2 , Eu_2O_3 , and DyO_3 .

[00026] The bonding layer is, for example, Keronite (surface coating treatment commercially available from Keronite Limited, Advanced Surface Technology, PO Box 700, Granta Park, Great Abington, Cambridge CB1 6ZY, UK). In general, the bonding layer can comprise three layers including: a thin transition layer between the (metal) processing element and the ceramics, a

dense primary layer that provides hardness, and a softer, more porous outer layer. The softer, more porous outer layer, which typically comprises up to 10 to 20% of the total bonding layer thickness, can be removed by polishing in order to provide a bonding surface for the application of the protective layer. Since the bonding layer, as described, is a conversion layer, it possesses improved adhesion properties due to molecular bonding.

[00027] FIG. 3 presents a method of forming the protective barrier on a processing element. The method is presented in flow chart 500 beginning with step 510, wherein the bonding layer is applied to at least one surface of the processing element. The processing element can, for example, be fabricated using at least one of machining, polishing, and grinding. For example, the processing element described above can be machined according to specifications set forth on a mechanical drawing, using conventional techniques including a mill, etc. The techniques for machining a component using, for example, a mill, are well known to those skilled in the art of machining such materials. The processing element can comprise at least one of a metal, a silicon based material, and a ceramic. The processing element can, for example, comprise aluminum. The bonding layer can comprise Keronite. For example, a Keronite layer can be formed via plasma electrolytic oxidation (PEO) that includes masking the processing element and submersing the processing element in a wet chemistry electrolytic bath for transforming the metallic surface into a hard, dense and adhesive ceramic by plasma discharge in the liquid electrolyte. Optionally, the (third) softer, more porous layer in the bonding layer can be removed by polishing.

[00028] In step 520, the protective layer is applied to the bonding layer. The protective layer comprising, for example Yttria, can be formed using (thermal) spray coating techniques that are well known to those skilled in the art of ceramic spray coatings. In an alternate embodiment, forming the protective barrier can further comprise polishing the thermal spray coating. For example, polishing the thermal spray coating can comprise the application of sand paper to the sprayed surfaces.

[00029] Although only certain exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without

materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention.

CLAIMS:

What is claimed is:

1. A protective barrier on a processing element utilized in a processing system for performing a process comprising:

a bonding layer coupled to said processing element, wherein said bonding layer comprises a layer formed using plasma electrolytic oxidation; and

a protective layer coupled to said bonding layer and configured to be exposed to said process.

2. The protective barrier as recited in claim 1, wherein said bonding layer comprises Keronite.

3. The protective barrier as recited in claim 2, wherein said Keronite comprises a transition layer, a primary layer, and an outer layer.

4. The protective barrier as recited in claim 3, wherein said protective layer is coupled to said bonding layer after at least a portion of said outer layer is removed using at least one of polishing, grinding, and grit blasting.

5. The protective barrier as recited in claim 1, wherein said protective layer comprises a compound containing at least one of a III-column element and a Lanthanum element.

6. The protective barrier as recited in claim 5, wherein said III-column element comprises at least one of Yttrium, Scandium, and Lanthanum.

7. The protective barrier as recited in claim 5, wherein said Lanthanum element comprises at least one of Cerium, Dysprosium, and Europium.

8. The protective barrier as recited in claim 1, wherein said protective layer comprises at least one of Al_2O_3 , Ytria (Y_2O_3), Sc_2O_3 , Sc_2F_3 , YF_3 , La_2O_3 , CeO_2 , Eu_2O_3 , and DyO_3 .

9. The protective barrier as recited in claim 1, wherein the processing element comprises at least one of a metal, a silicon based material, and a ceramic.

10. The protective barrier as recited in claim 1, wherein the processing element comprises aluminum.

11. The protective barrier as recited in claim 1, wherein the process comprises a plasma.

12. A method of forming a protective barrier on a processing element utilized in a processing system for performing a process comprising:
applying a bonding layer to said processing element, wherein said application of said bonding layer comprises plasma electrolytic oxidation; and
applying a protective layer to said bonding layer.

13. The method as recited in claim 12, wherein said bonding layer comprises Keronite.

14. The method as recited in claim 13, wherein said Keronite comprises a transition layer, a primary layer, and an outer layer.

15. The method as recited in claim 14, wherein said outer layer is removed using at least one of polishing, grinding, and grit blasting.

16. The method as recited in claim 12, wherein said protective layer comprises a compound containing at least one of a III-column element and a Lanthanum element.

17. The method as recited in claim 16, wherein said III-column element comprises at least one of Yttrium, Scandium, and Lanthanum.

18. The method as recited in claim 16, wherein said Lanthanoid element comprises at least one of Cerium, Dysprosium, and Europium.

19. The method as recited in claim 12, wherein said protective layer comprises at least one of Al_2O_3 , Yttria (Y_2O_3), Sc_2O_3 , Sc_2F_3 , YF_3 , La_2O_3 , CeO_2 , Eu_2O_3 , and DyO_3 .

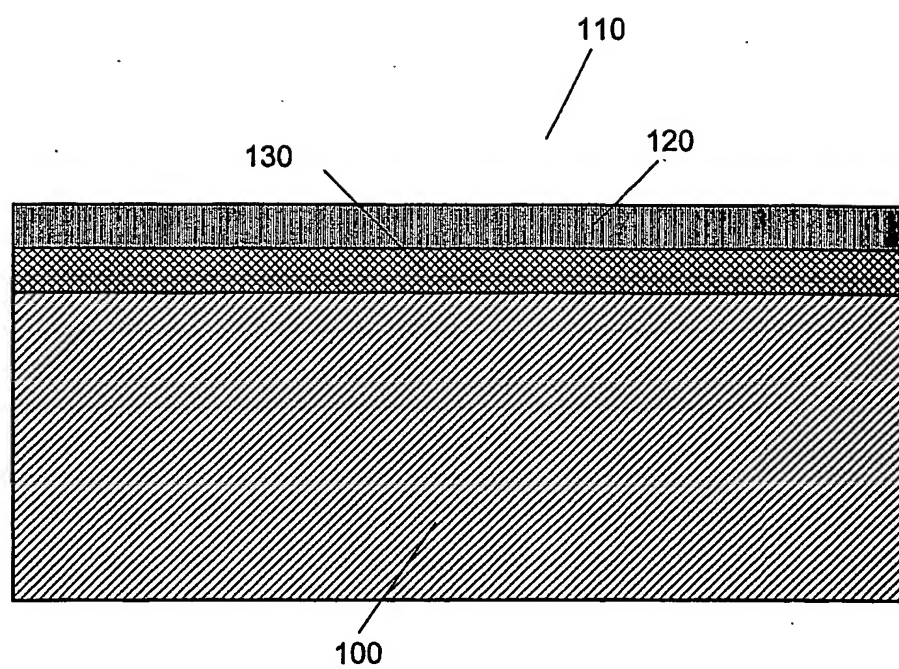


FIG. 2.

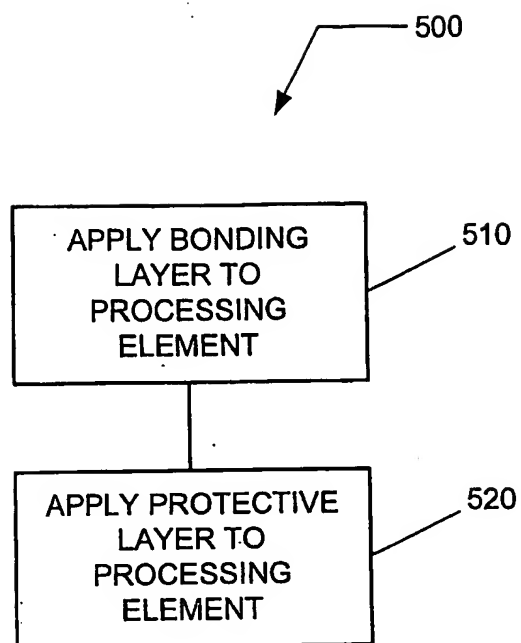


FIG. 3.